25X1A [redacted]

RESTRICTED
SECURITY INFORMATION

FOREIGN DOCUMENTS DIVISION

25X1A [redacted]

31 March 1953

Is There a Higher Peroxide of Hydrogen?

by N. M. Emanuel' and K. E. Krugliakova

Priroda, No 6, pp 103-105, June 1952, Russian mo per, Moscow

(This report has not been edited or prepared for publication)

RESTRICTED

RETURN TO CIA LIBRARY

Approved For Release 1999/09/10 : CIA-RDP83-00423R001200170004-6

DOES THERE EXIST A HIGHER HYDROGEN PEROXIDE?

Professor N. M. Emanuel' and

K. E. Kruglyakova

From: Priroda [Nature], No 6, June 1952, pp 103-105

Somewhat more than 50 years ago the outstanding Russian chemist, A. N. Bakh, made the statement that, together with ordinary hydrogen peroxide H_2O_2, there also exists a higher hydrogen peroxide with the composition H_2O_4. A. N. Bakh conducted a number of experiments to confirm his point of view. These experiments did not encounter any support during his time. Moreover, certain foreign scientists expressed themselves against them. Since that time the question of the higher hydrogen peroxide has been raised very rarely in chemical literature.

Hydrogen peroxide is a product which has wide usage in industry, technology, and medicine. It also plays a great role in processes taking place in living organisms. It is not by chance that biochemists call hydrogen peroxide the most important

peroxide of biological significance. It is clear therefore that the question of the existence of a higher hydrogen peroxide cannot fail to be of considerable interest to chemistry. But along what path ought we to seek proof of the existence of this compound?

A. N. Bakh himself made direct indications of the path of research. In 1897 he wrote, ". . . I had a certain foundation for assuming that when hydrogen oxidizes, at the moment that oxides are formed, there can also form a higher peroxide, namely, a hydrogen tetroxide H-O-O-O-O-H, derived from the joining of two

incomplete groups H-O-O- and -O-O-H" (A. N. Bakh, Sobraniye trudov po khimii i biokhimii [Collected Works on Chemistry and Biochemistry], Izd-vo AN SSSR [Publishing House of the Academy of Sciences USSR], 1950, page 253). For that time this was a very daring assumption. A. N. Bakh assumed that when hydrogen oxidizes there are formed "incomplete groups", that is, molecular fragments. These fragments, joining together, form an ordinary, so-called "saturated" molecule. Nowadays chemists are no longer surprised by the existence of "incomplete groups", which are called free radicals. When research was being conducted on the course of many chemical reactions, it was discovered that, as these reactions proceed, free radicals are formed. The peculiarity of these radicals consists in the fact that they exist for a short time, because, meeting one another, they are converted into saturated molecules. Therefore it is very difficult to discover and study free radicals. A. N. Bakh was far

ahead of his time when he assumed that a free radical HO_2 is formed under certain conditions. After Bakh, chemists began to make use of the idea of the existence of the HO_2 radical when attempting to investigate the chemical mechanisms of various complex reactions. Nonetheless, to the present day no one has proven with sufficient conviction that the HO_2 radical actually does exist.

On the basis of what has been stated, the following path of study was outlined. It was necessary to study the reactions in which the formation of the HO_2 radical was probable and to attempt to discover, during these reactions, the H_2O_4 compound.

Positive results would have served as proof of the existence of a higher hydrogen peroxide and the existence of the HO_2 radical. Proof of either is very important to chemistry and the special branch of chemistry which studies the mechanism of chemical reactions and the laws governing their passage in time (so-called chemical kinetics).

Following this idea we undertook in our laboratory to study the reaction of the decomposition of hydrogen peroxide.

It is generally well-known that hydrogen peroxide decomposes easily, releasing oxygen and forming water by the reaction: $2H_2O_2 = 2H_2O + O_2$. The reaction of the decomposition of H_2O_2 is greatly accelerated by infinitesimal additions of various admixtures -- catalysts: metallic salts, metals in colloid condition, powdered glass, cotton, etc. It is also accelerated by the action of light and increased temperature. Together with this it is well-known that small additions of certain substances can prevent decomposition even under conditions in which it ordinarily proceeds vary intensively. These additions are called stabilizers of hydrogen peroxide or inhibitors of the reaction of its decomposition. They include, for example, many organic compounds -- alcohols, acids, etc.

There is a class of chemical conversions for which the phenomena listed above are typical. We are speaking of so-called chain reactions. The mechanism of chain reactions is as follows. In a system which is capable of chemical conversion at a slow rate of speed there form active substances -- atoms or radicals. These

active particles possess a very high capacity for reacting. They easily take part in chemical reaction with the molecules of the initial substances, as a result of which there arises a molecule of the final product plus a new atom or radical which is able to take part in a new reaction, etc. Consequently, one originally formed active center can cause a long chain of chemical conversions. This chain chemical conversion is ended by a process which leads to the annihilation of the active particle. This scheme of the passage of the chemical process easily explains the effects of the action of small amounts of various catalysts, the influence of light, etc. If the addition of some substance can contribute to the increase in the number of active particles in the system, then this substance will accelerate the chemical reaction. If, on the other hand, the active centers die when they come in contact with the molecules of the substance added, then this substance will be an inhibitor of the chain reaction. Only infinitesimal amounts of a catalyst or inhibitor are needed to greatly influence the reaction.

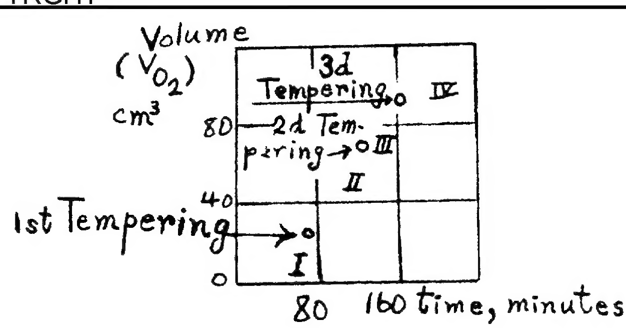

Figure 1. Release of oxygen during the decomposition of solution of hydrogen peroxide in water, at a temperature of 90 degrees Centigrade.

The action of light is explained in exactly the same way. If, with the influence of light upon a molecule, active centers can form, then light will accelerate the reaction. Ordinarily the action of light upon a chemical reaction is characterized by the quantum yield of the reaction -- the number of molecules of the final product when the system absorbs one quantum of light (light particle). In chain reactions the quantum yields of the reaction, as a rule, are very great. A large quantum yield is also observed for the reaction of the decomposition of hydrogen peroxide.

Fairly long ago the conclusion was made that the decomposition of hydrogen peroxide is a chain reaction and an assumption was made concerning very probable chemical reactions with the participation of molecular fragments -- radicals -- which are the cause of the chain of conversions. The chemical mechanism of the chain reaction of the decomposition of H_2O_2 includes the reactions of two radicals of OH (free hydroxyl) and the HO_2 radical. If, as the result of some reaction, the OH or HO_2 radical is formed in the system, it causes a chain of conversions according to the scheme:

$$OH + H_2O_2 = H_2O + HO_2$$

$$HO_2 + H_2O_2 = H_2O + O_2 + OH \text{ etc.}$$

The final products of this assumed chain reaction are precisely the same products which we observe in practice: water and oxygen. With regard to the OH and HO_2 radicals, no one has discovered them in this reaction.

Thus the reaction of the decomposition of H_2O_2 is very

suitable for our purposes. If the HO_2 radical is actually formed in the system, then it is possible that, as the result of the joining of two HO_2 radicals, a higher hydrogen peroxide H_2O_4 is formed.

The authors of this report have studied the reaction of the decomposition of pure (without any admixtures) solutions of hydrogen peroxide in water.

The course of the reaction in time can be observed very conveniently by the release of oxygen. Because at room temperature the reaction takes place very slowly, the H_2O_2 solutions were heated to 90 degrees Centigrade. Figure 1 shows how the amount of oxygen, formed by the decomposition of H_2O_2, increases in time. It is obvious from the drawing that at first the oxygen is released slowly, then more and more quickly, and, finally, slowly again (because of the decrease in the amount of hydrogen peroxide). In the course of these experiments, the following remarkable phenomenon was noted. If the reaction of decomposition is stopped by cooling the vessel with cold water (this operation is called "tempering"), and then the vessel is again heated to 90 degrees, the reaction continues with the same speed as if the cooling had not taken place.

"Tempering" can be done several times during the course of one experiment and every time, after each "tempering" in turn, the reaction continues, instead of beginning again. This result could be obtained only if the active centers formed in the course of the reaction do not die when "tempered", but retain their active capacity until the experiment is repeated. This is a very

surprising result, because it is well-known that when a reaction is stopped, free radicals are quickly annihilated, because they join with one another (recombination).

Then wherein lies the reason why partially decomposed hydrogen peroxide retains its chemical activity? Can it be that the product of the joining of radicals, with repeated heating, again decomposes easily into radicals? OH radicals, joining one another, yield H_2O_2 (from two OH radicals), that is, the initial product. Consequently, this process cannot lead to the preservation of chemical activity.

The circumstance may be different with an HO_2 radical. When these radicals join, a compound H_2O_4 is formed. This compound must be very unstable and consequently, the result which we obtained is completely understandable. When "tempered", H_2O_4 is formed from HO_2, and when heated a second time, the H_2O_4 decomposes into two HO_2 radicals and the chain reaction continues as if this tempering had not been made at all. It was possible to foresee yet another phenomenon. Let us assume that the HO_2 radical, in the course of the reaction, is formed in considerable quantities. Then, by conducting a "tempering" in the course of the reaction and determining the remaining undecomposed amount of hydrogen peroxide, we must note that the amount of released oxygen will be less than we should have expected, judging by the decomposed hydrogen peroxide. Part of the oxygen would be retained in the form of H_2O_4, formed by the joining of two HO_2 radicals. We actually succeeded in observing the phenomenon of insufficient release of oxygen. The value of

incomplete release is measured regularly during the course of the reaction (Figure 2) and reaches 10 cubic centimeters of oxygen (this comprises approximately 10 percent of the complete amount of O_2 which can be released when the initial hydrogen peroxide is completed decomposed. Since each incompletely released molecule of O_2 is retained in the higher hydrogen peroxide H_2O_4, for the formation of which 2 HO_2 radicals are expended, it is natural that the amount of HO_2 radicals will be equal to the doubled number of incompletely released molecules of oxygen.

Ordinarily, free radicals are formed in chemical reactions in small amounts. Exceptions are only the so-called chain, branched reactions, characterized by the progressive increase in the number of active centers (atoms and radicals) in the course of the process. In these reactions the amount of the least active radicals can reach tens of percent of the amounts of the initial substances. On this basis it can be thought that the reaction of the decomposition of H_2O_2 is a chain, branched reaction. Our experiments have further shown that, when decomposing hydrogen peroxide solutions of identical composition by percent, prepared by diluting concentrated solutions with water -- once immediately after obtaining the peroxide, and another time a month after obtaining it -- different amounts of oxygen are derived when the solutions are completely decomposed. In the second instance, more oxygen is released. It is clear that in the peroxide kept for a month at room temperature, a slow process of decomposition had been going on. The relatively inactive HO_2 radicals which were formed could not, because of the low temperature, take part

in the reaction with hydrogen peroxide, and joined into H_2O_4, which, when decomposed, gives more oxygen than H_2O_2.

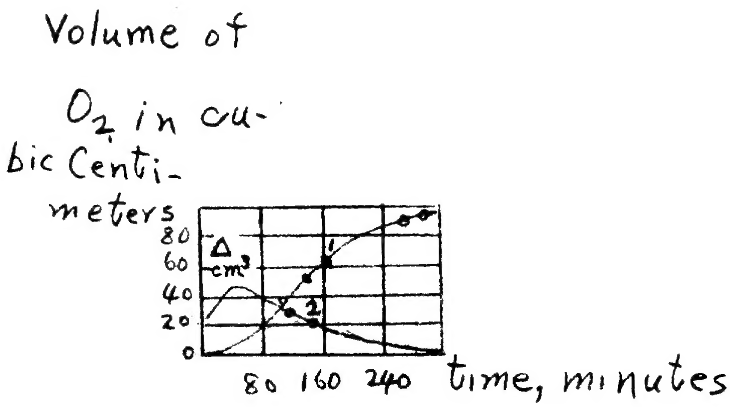

Figure 2. The phenomenon of incomplete release of oxygen during the decomposition of solutions of hydrogen peroxide in water, at a temperature of 90 degrees Centigrade. 1 - Release of oxygen, observed in the experiment. 2 - Incomplete release of oxygen, computed by proceeding from data on the amount of decomposed hydrogen peroxide and the amount of released oxygen.

Let us also note that recently, Soviet scientists K. V. Astakhov and A. G. Getsov reported the fact, discovered by them, that oxygen is gradually released from a solution by the interaction of a compound of CaO_4 and dilute acid. They explain this fact by the existence of an HO_2 compound in the solution. Unfortunately the authors did not, in their report, introduce any

experimental data with regard to the interesting observation made by them. Nonetheless it is evident that one must also see in the report of K. V. Astakhov and A. G. Getsov an indication of the existence of a higher hydrogen peroxide.

The results derived by us make it possible again to speak about the higher hydrogen peroxide of A. N. Bakh, and about the existence of the HO_2 radical, and to raise anew the question of the chain mechanism of the decomposition of hydrogen peroxide.

It is necessary to continue research of the higher hydrogen peroxides, which research is of considerable interest to chemistry.

Institute of Chemical Physics of the Academy of Sciences USSR

RESTRICTED CONFIDENTIAL SECRET

ROUTING AND CONTROL RECORD

DO NOT DETACH FROM 'ON LOAN' DOCUMENTS

25X1A [redacted]

DATE

TO:
CIA Library

ATTN:

BUILDING	ROOM NO.

TITLE

"IS There a Higher Peroxide of Hydrogen?"

REMARKS

25X1A
[redacted]

25X1A

xxxx RETAIN	ON LOAN
DOCUMENT(S) FOR RETENSION BY ADDRESSEE	DOCUMENT(S) MUST BE RETURNED TO CONTACT DIVISION/[redacted]
	BY (DEADLINE) 25X1A 25X1A

FROM: CONTACT DIVISION/[redacted]

BRANCH [redacted]

BUILDING	ROOM NO.	EXTENSION
South	300	2491

SECRET CONFIDENTIAL RESTRICTED

FORM NO. 57-29
DEC 1951

(20-40)

TRA !SMITTAL SLIP

25X1A (Date)

TO: [redacted]

BUILDING | ROOM NO.

REMARKS:

This Report is unclassified without the cover sheet

FROM:

BUILDING | ROOM NO. | EXTENSION

FORM NO. 36-8
SEP 1946

16—65268-1 GPO